Chapter 2

Binary approach

This chapter presents the details about experimental techniques and theoretical approaches/model used in this study. First part, experimental methodology, covers the bulk and thin film synthesis, experimental techniques used for characterization and details of irradiation phenomenon. Second part, theoretical formalisms, explains the details of specific heat analysis including the description of lattice contribution and theoretical background of Rietveld refinement technique used for structural refinement.
2.1 Experimental methodology

2.1.1 Synthesis of bulk materials

Bulk multiferroic samples used in the present study have been synthesized using solid state reaction method. The typical procedure for exchange of ions in the solid state is very simple, involving heating a mechanical mixture of transition metal oxide (or salt) in a stream of inert gas, under vacuum, or in air. The temperature at which the solid-state exchange reaction reaches an appreciable rate depends on the type of cation and anion. This technique has been even proven to be a unique method for introducing transition metal cations in high-silica zeolites [69].

The solid-state reaction technique mainly involves four major steps (i) Mixing of the required oxide/carbonate powders in stoichiometric proportion, (ii) Calcination, (iii) Pelletization and (iv) Sintering of the polycrystalline bulk. The solid-state reaction used for the preparation of BiMn$_{2-x}$Ti$_x$O$_5$ sample is given as follow:

$$(0.5) \text{Bi}_2\text{O}_3 + (2-x) \text{MnO} + (x) \text{TiO}_2 \rightarrow \text{BiMn}_{2-x}\text{Ti}_x\text{O}_5$$ (2.1.1)

For the preparation of bulk BiMn$_{2-x}$Ti$_x$O$_5$ ($0 \leq x \leq 0.5$) multiferroic samples, the high purity (~ 99.99 %) fine powders of AR grade of Bi$_2$O$_3$, MnO and TiO$_2$ were weighed and mixed in stoichiometric proportion. The quantities of the reagents required for this composition was calculated from the above mentioned solid-state reaction technique for 5g of each sample. The powders weighed in the appropriate proportion were mixed thoroughly and ground using a mortar and pestle. This process was carried out at least for one hour in order to accomplish the homogeneity of the mixed powder.

The decomposition of the mixed powder by heating below its melting point is known as calcination. The intention of calcination procedure is to establish the course of nucleation for the grain growth and felicitates the decomposition of the substituent oxides/carbonates. Mixed powders were kept in a crucible and heated in the furnace at 800°C for 12 hours to ensure that all the hydrides and carbides are liberated from the mixture.
In order to make use of these ceramic materials, the calcinated powders must be brought into the required shapes and densities, before the final sintering process. This is achieved by using die-press technique in which a die of proper shape was filled with calcinated powder and pressed using hydraulic press. In our case, pelletization is done in a die of circular shape of 15 mm diameter and the pressure applied was ~ 6 Ton.

After pelletization of the fine calcinated powder, sintering of the pellet is done at relatively higher temperature and for longer duration used during calcination. This is followed by slow cooling with a suitable predefined rate, which is an essential and important process as it maintains the required oxygen content in the material. The final sintering is done at 840°C for 24 hours in a furnace followed by slow cooling to room temperature. This heat-treatment procedure was repeated for three times to get better homogeneity in the samples.

2.1.2 Thin film deposition using Pulsed Laser Deposition (PLD) technique

PLD was used to prepare BiMn$_2$O$_5$ thin films on LaAlO$_3$ (LAO) substrates. In the PLD technique, a laser beam (an excimer laser) is directed at a solid target. The interaction of the pulsed laser beam with the target produces a plume of material that is transported toward a heated substrate placed directly in the line of the plume.

Theoretically and experimentally PLD is a simple thin film deposition technique. There is one rotating target holder and one substrate holder facing each other in a stainless steel vacuum chamber. A high energy pulsed laser beam (most frequently an excimer laser) is used as an external energy source to vapourize materials from the target surface. A set of optical lenses is used to focus the laser beam on the target surface. A schematic diagram of a PLD vacuum chamber is shown in Fig. 2.1.1. The pulsed laser beam typically has 30 ns pulses with energy in the range of 0.01-1.2 J and at a frequency of 1-20 Hz. As a result, the plume which contains materials ablated from the target is ejected normal to the target surface. The plume expands away from the target with a strong forward-directed velocity.
distribution of the different particles. The ablated species condense on the substrate placed opposite to the target. The ablation process in the vacuum chamber takes place either in vacuum or in the presence of some gas. In the case of oxide films, oxygen is the most common gas.

![Fig. 2.1.1 Schematic diagram of PLD system.](image)

The principle of PLD, in contrast to the simplicity of the system set-up, is a very complex physical phenomenon. It not only involves the physical process of the laser-material interaction on a solid target and energy transformation, but also the formation of the plasma plume with high energetic species and the transfer of the ablated material through the plasma plume onto the heated substrate surface [70]. Generally, the PLD process can be divided into the following four steps: 1) interaction of laser with the target; 2) dynamics of the ablation materials; 3) deposition of the ablation materials on the substrate; and 4) nucleation and growth of a thin film on the substrate surface. Each of the above steps is critical to the quality and characteristics of the films i.e. crystallinity, stoichiometry, uniformity, and surface roughness. During deposition, different parameters including
substrate temperature, laser energy density and frequency, target-to-substrate distance, base pressure and deposition gas pressure are optimized to achieve high quality thin films. The substrate temperature is critical to the crystallinity of the films. Normally, an amorphous phase forms when the substrate temperature is below a certain value. As the substrate temperature increases, films start to crystallize. For an epitaxial growth, the substrate temperature should be optimized, which varies for different materials. The energy density of the laser beam has significant effects on the uniformity of the film. Target-to-substrate distance is a parameter that governs the angular spread of the ablated materials. The oxygen partial pressure is also a very important parameter in the growth of oxide films. The chamber is normally pumped down to a base pressure of \( \sim 10^{-5} \) Torr before the reactive gas, such as oxygen, is introduced into the chamber. The lasers commonly used for PLD include ArF, KrF, XeCl and XeF excimer lasers with wavelength of \( \lambda = 193, 248, 308, \) and 351 nm, respectively. It is generally recognized that the shorter is the wavelength, the more effective is the laser ablation process.

The most important feature of PLD is that the stoichiometry of the target can be retained in the deposited films. This is the result of the extremely high heating rate of the target surface due to pulsed laser irradiation. Because of the very short pulse width of the laser, the evaporation of the target is negligible. When the target material is ejected towards the substrate, different components have similar deposition rates, making the film with same composition as the target material. Another advantage of the PLD is its versatility. With the choice of an appropriate laser almost any material can be deposited in a wide variety of gases over a broad range of gas pressures and substrate temperatures. The targets used in PLD are small compared to the large size required for sputtering techniques. It is quite easy to produce multi-layered films of different materials by sequential ablation of assorted targets held in one target holder. Also, by controlling the number of pulses, fine control of film thickness down to the monolayer can be achieved. Another advantage of PLD is its cost-effectiveness. Several vacuum chambers can be arranged around a single laser source and the laser beam can be directed to each chamber using different mirrors and lenses. There are, however, two major disadvantages associated the use of PLD. One is the lack of uniformity over a large area which is due to the narrow angular distribution of the plume.
The other and most important disadvantage is an intrinsic problem called “splashing” which results in deposition of micron sized particulates on top of the film surface. The occurrence of splashing has several origins such as surface boiling, expulsion of liquid by shockwave recoil, and exfoliation [71]. There are several solutions to avoid splashing which include using a high quality target, target surface improvement and smoothing, mechanical particle filter, plume manipulation, off-axis PLD and lowering laser energy density. With respect to scaling-up due to the demand for metal-oxide based electronics or other multicomponent thin films, the commercial-scale development of PLD systems is possible. It has been reported [72] that some PLD systems can deposit thin films on 8-inch wafers with deposition rates of more than 1 micron-cm²/s.

In this study, a pulsed KrF (wavelength = 248 nm) excimer laser was used for ablation (repetition rate of 5 Hz and energy density of 1.7 J/cm²). The chamber was evacuated to base pressure of 1x10⁻⁶ Torr and deposition was carried out at 100 mTorr of oxygen background pressure. The deposition was performed at 500 °C for 40 mins. The thickness of all the films are around 200 nm as measured by stylus profilometer.

2.1.3 X-ray diffraction

X-ray diffraction (XRD) is a powerful method, which is widely used for the characterization of crystalline and structural properties. When monochromatic X-ray radiation is incident upon the sample, a part of the radiation is scattered from the sample atoms. Scattered X-rays constructively interfere when certain conditions are satisfied. This phenomenon is known as diffraction of X-rays. The path difference between the x-rays scattered from two adjacent planes is related with the interatomic plane distance \( d_{\text{hkl}} \) and the incident angle \( \theta \). If the travelling difference is equal to an integer number of the incident X-ray wavelength then the constructive interference of the diffracted beam occurs and a sharp diffraction peak can be observed, which is expressed by Bragg’s Law [Eq. (2.1.2)]:

\[
 n\lambda = 2d \sin \theta \tag{2.1.2}
\]
where \( n \) is an integer, \( \lambda \) is the wavelength of X-rays (generally, Cu K\(_\alpha\) (1.54056 Å)), \( d \) is the interplaner spacing and \( \theta \) is the diffraction angle.

Typical diffractometers use either 3- or 4-circle goniometers. These circles refer to the four angles (\( 2\theta, \chi, \phi, \) and \( \omega \)) that define the relationship between the crystal lattice, the incident ray and detector. Samples are mounted onto goniometer heads. Adjustment of the X, Y and Z orthogonal directions allows centering of the crystal within the X-ray beam. The typical XRD measurement techniques are schematically illustrated in Figure 2.1.2.

![Fig. 2.1.2 Schematic of XRD measurement techniques.](image)

In this study, XRD measurements were carried out by Rigaku diffractometer and Bruker D8 with monochromatized Cu K\(_\alpha\) radiation. A typical \( \theta - 2\theta \) scans were performed in the XRD studies.
2.1.4 Dielectric measurement

The dielectric constant for the bulk sample was calculated by measuring the capacitance of the material. The capacitance as a function of frequency and temperature was measured using Agilent 4284A precision LCR meter. Shielded test leads were used for the electrical connections from the analyzer to the sample in order to avoid any parasitic impedance. The samples were made in the form of circular pellets by applying a pressure of 6 tons. Before starting the measurement the samples were heated at 100 °C for 1 hour, so as to homogenize the charge carriers and to remove the moisture content, if any. The surface of the pellets were polished and coated with silver paste, which acts as a good contact for measuring the dielectric properties. For temperature dependent dielectric measurements, we have used a closed cycle refrigerator (CCR) setup that enables us to measure the dielectric constant in the temperature range of 10 – 300 K.

The value of the dielectric constant ($\varepsilon'$) was calculated using the formula;

$$\varepsilon' = \frac{C}{C_0}$$  \hspace{1cm} (2.1.3)

where $\varepsilon'$ is the real part of the dielectric constant, $C$ is the capacitance of the material inserted between the electrodes and $C_0$ is the capacitance of the medium as air or no medium between the electrodes. The $C_0$ for the parallel plate capacitor can be calculated using the following relation

$$C_0 = \frac{\varepsilon_0 A}{t}$$  \hspace{1cm} (2.1.4)

where $\varepsilon_0$ is permittivity in vacuum $\sim 8.854 \times 10^{-12}$ C$^2$/N.m$^2$, $t$ is the sample thickness and $A$ is the area of the specimen in sq. m.

Using eq. 2.1.3 and 2.1.4, the dielectric constant can be calculated as

$$\varepsilon' = \frac{C \times t}{\varepsilon_0 \cdot A}$$  \hspace{1cm} (2.1.5)

The imaginary component of dielectric constant ($\varepsilon''$) is calculated using the formula;

$$\varepsilon'' = \varepsilon' \tan \delta$$  \hspace{1cm} (2.1.6)

where $\tan \delta$ is loss tangent, proportional to the ‘loss’ of energy from the applied field into the sample (in fact, this energy is dissipated into heat) and therefore denoted as dielectric loss.
2.1.5 Magnetic characterization

(i) Vibrating sample magnetometer (VSM)

The vibrating sample magnetometer (VSM) is the most commonly used instrument for measurements of the magnetic properties of the samples. VSM was developed in 1956 by S. Foner and Van Oosterhart [73]. The principle behind the measurement is simple: it uses an electromagnet which provides a DC magnetizing field. When a material is placed within a uniform magnetic field, a vibrator mechanism vibrates the sample in the magnetic field. This causes the sample to undergo sinusoidal motion and creates a change in the magnetic flux, which is detected by pickup coils as an induction voltage. The flux change is proportional to the magnetic moment in the sample:

\[ V(t) = C \frac{d\phi(t)}{dt} \quad (2.1.7) \]

where \( \phi(t) \) represents the change in flux in the pick-up coils caused by the moving magnetic sample. The output measurement displays the magnetic moment \( M \) as a function of the field \( H \).

Fig. 2.1.3: An illustration of Vibrating Sample Magnetometer
A schematic of the VSM system is shown in Fig. 2.1.3. VSM provides a fast and easy technique for the measurement of the magnetic properties of a material.

In the present study, VSM option of Physical Property Measurement Setup (PPMS) made by Quantum design has been used for the magnetization measurement of bulk BiMn$_2$-$_x$Ti$_x$O$_5$ (0 $\leq$ x $\leq$ 0.5) multiferroic samples from 5 K to the room temperature. The sensitivity of VSM manufactured by Quantum design is in the range of $10^{-4}$ emu.

(ii) Superconducting Quantum Interference Device (SQUID) magnetometer

To measure the hysteresis loop and susceptibility more accurately and at lower temperatures, a Superconducting Quantum Interference Device (SQUID) magnetometer was used. SQUIDs are very sensitive detectors of magnetic flux. They combine the physical phenomena of flux quantization and Josephson tunneling. A Josephson junction consists of two weakly coupled superconducting electrodes which are separated by a thin insulating barrier. If superconductors separated by a thin insulating layer are brought very close to each other, tunneling of electrons can occur. If the distance is reduced even more, tunneling of Cooper-pairs will also occur. For currents below a critical value, the pair tunneling constitutes a supercurrent, and no voltage is developed across the junction. However, a voltage appears for currents greater than the critical value. The presence of the insulating layer typically restricts the value of the supercurrent flowing in the coil to less than $10^{-5}$ A. Most of the low-Tc SQUIDs are made from Niobium thin films which have a transition temperature around 9.25 K, well above the boiling temperature of liquid helium and are also mechanically very stable. Tunnel junctions are patterned from Nb/AlO$_x$/Nb trilayers in which a AlO$_x$ barrier is formed by oxidization of a few nanometers of aluminum [74]. Fig. 2.1.4 shows a schematic of a Josephson junction [75].
Fig. 2.1.4 Schematic of a Josephson junction consisting of two superconductors separated by thin insulating layers.

There are two types of SQUIDs. The first, DC SQUID, consists of two Josephson junctions connected in parallel on a superconducting loop and is operated in the voltage state with a current bias. The second kind, RF SQUID, consists of a single Josephson junction inserted into a superconducting loop. The sample is placed in a superconducting pick-up coil that is connected to the actual SQUID. Since the magnetic flux through a superconducting ring is quantized to $f = nf_0$ with $f_0 = h/(2|e|)$ where $n$ is an integer, $h$ is Planck's constant and $e$ is electron charge, the sample will induce a supercurrent in the pick-up coils that will keep the flux at a constant value.

In the present study magnetic properties of pristine and irradiated thin films were characterized using Quantum Design MPMS SQUID Magnetometer. A sensitivity of $10^{-7}$ emu is claimed by Quantum Design (the manufacturer) but sensitivity of $10^{-6}$ emu is typically seen in practice. The temperature can be varied between $T = 1.7$ and 400 K.


2.1.6 X-ray absorption spectroscopy (XAS)

(i) X-ray absorption fine structure (XAFS)

X-ray absorption spectroscopy (XAS) refers to the details of how x-rays are absorbed by an atom at energies near and above the core-level binding energies of that atom. When the x-rays hit a sample, the oscillating electric field of the electromagnetic radiation interacts with the electrons which are bound in an atom. Either the radiation will be scattered or absorbed by these electrons, which causes excitation of the electrons. Schematic x-ray absorption phenomenon is shown in Fig. 2.1.5. A narrow parallel monochromatic x-ray beam of intensity $I_0$ passing through a sample of thickness $x$ will get a reduced intensity $I$ according to the expression:

$$\ln \left( \frac{I_0}{I} \right) = \mu x \quad (2.1.8)$$

where $\mu$ is the linear absorption coefficient, which depends on the type of atom and the density $\rho$ of the material. At certain energies where the absorption increases drastically, gives rise to an absorption edge.

![Schematic x-ray absorption phenomenon](image)

Each such edge occurs when the energy of the incident photon is just sufficient to cause excitation of a core electron of the absorbing atom to a continuum state, i.e. to produce a photoelectron. Thus, the energies of the absorbed radiation at these edges correspond to the
binding energies of electrons in the K, L, M, etc., shells of the absorbing elements. The absorption edges are labelled in the order of increasing energy, K, L\(_1\), L\(_{10}\), L\(_{11}\), M\(_1\), etc., corresponding to the excitation of an electron from the 1s (S\(_{1/2}\)), 2s (S\(_{1/2}\)), 2p (P\(_{3/2}\)), 2p (P\(_{1/2}\)), 3s (S\(_{1/2}\)), ... orbitals (states), respectively.

![X-ray absorption spectrum](image)

**Fig. 2.1.6.** X-ray absorption spectrum in pre-edge, XANES, NEXAFS and EXAFS regions.

An x-ray absorption spectrum is generally divided into 4 sections (see Fig. 2.1.6): (1) pre-edge (E < E\(_0\)); (2) x-ray absorption near edge structure (XANES), where the energy of the incident x-ray beam is E = E\(_0\) ± 10 eV; (3) near edge x-ray absorption fine structure (NEXAFS), in the region between 10 eV up to 50 eV above the edge; and (4) extended x-ray absorption fine structure (EXAFS), which starts approximately from 50 eV and continues up to 1000 eV above the edge. The minor features in the pre-edge region are usually due to the electron transitions from the core level to the higher unfilled or half-filled orbitals (e.g., s → p, or p → d). In the XANES region, transitions of core electrons to non-bound levels with
close energy occur. Because of the high probability of such transition, a sudden rise in absorption process is observed. In NEXAFS, the ejected photoelectrons have low kinetic energy \( (E-E_0 \) is small) and experience strong multiple scattering by the first and even higher coordinating shells. In the EXAFS region, the photoelectrons have high kinetic energy \( (E-E_0 \) is large) and single scattering by the nearest neighboring atoms normally dominates.

In the present work, NEXAFS measurement has been done at O- K, Mn-L\(_{3,2}\) and Ti-L\(_{3,2}\)-edges of bulk BiMn\(_x\).Ti\(_x\)O\(_5\) (0 ≤ \(x\) ≤ 0.5) along with other reference compounds at the soft x-ray beam line 7B1 KIST of the Pohang Accelerator Laboratory (PAL), Korea, operating at 2.5 GeV with a maximum storage current of 200 mA and for Mn-K edge, BL7C1 beamline of the Pohang Light Source (PLS) was utilized. For pristine as well irradiated thin films of BiMnO\(_5\), NEXAFS measurements have been performed at the (European Synchrotron Radiation Facility) ESRF’s ID08 beamline, which uses an APPLE II type undulator giving ~100 % linear/circular polarization. All scans were collected simultaneously in both total electron yield (TEY) and total fluorescence yield (TFY) modes, ensuring both surface and bulk sensitivities.

(ii) X-ray magnetic circular dichroism (XMCD)

In optics, the term "dichroism" refers to changes in the absorption of polarized light on passing through a material in two different directions. First verification of XMCD was done in 1987 by Schutz et al. [76] and thereafter this technique in XAS has become a widely useful tool as a probe for the element-specific characterization of magnetic materials. The growing interest in XMCD stems partly from the growing availability of tunable high brilliance x-rays (synchrotron) and is partly from the unique possibility to analyze the magnetic moments not only element specific, but also separated into their spin and orbital contributions. The concepts of XMCD are illustrated in Fig. 2.1.7 [77]. Simple sum rules can be used to separate out the spin and orbital contributions to the magnetism [78, 79]. The first x-ray absorption sum rule links the total intensity of the L\(_3\) and L\(_2\) resonances with the N number of empty d states (holes). The d valence shell can hold up to 10 electrons which are filled into band states up to the Fermi level and the number of filled states is therefore 10
-N. For a magnetic material the d shell has a spin moment which is given by the imbalance of spin-up and spin-down electrons or equivalently (except for the sign) by the imbalance of spin-up and spin-down holes. In order to measure the difference in the number of d holes with up and down spin, we need to make the x-ray absorption process spin dependent. This is done by the use of right or left circularly polarized photons which transfer their angular momentum to the excited photoelectron.

Figure 2.1.7 represents the electronic transitions in conventional L-edge x-ray absorption (a), and x-ray magnetic circular x-ray dichroism (b, c), illustrated in a one-electron model. The transitions occur from the spin-orbit split 2p core shell to empty conduction band states. In conventional x-ray absorption, the total transition intensity of the two peaks is proportional to the number of d holes (first sum rule). By use of circularly polarized x-rays, the spin moment (b) and orbital moment (c) can be determined from linear combinations of the dichroic difference intensities A and B, according to other sum rules.

Fig. 2.1.7 Concepts of XMCD [77].
To separate the spin and the orbital part of the magnetic moment contribution of transition metal (TM), following formulae is used as per sum rule [78, 79]:

\[
\langle L_z \rangle = \frac{2(A + B)}{3C} \, n_h \tag{2.1.9}
\]

\[
\langle S_z \rangle = \frac{(A - 2B)}{2C} \, n_h \tag{2.1.10}
\]

In the above equations, \( A \) and \( B \) are the areas under the L3- and L2-edge respectively for the XMCD curves. \( C \) in the above equations is the area under the L3,2-edge XANES spectra and \( n_h \) is the number of holes in the 3d orbital of TM. Here we have neglected the magnetic dipole operator component. The error introduced in the calculations due to this and other sources, like in determination of background, rate of circular polarization and the number of electrons/holes in the 3d orbital are less than ~ 10 %.

In the present study, temperature dependent XMCD spectra at Mn L edges for pristine as well as irradiated BiMnO thin films have been performed at the ESRF’s ID08 beamline, which uses an APPLE II type undulator giving ~ 100 % linear/circular polarization.

2.1.7 Specific heat measurement

Specific heat in the simplest form is the amount of heat required to increase the temperature of a material by a unit amount. Depending on whether the pressure or the volume is kept constant, the specific heat is shown by \( C_p \) or \( C_v \) respectively. In our measurements the pressure is kept constant, hence \( C_p \) is measured.

Specific heat measurements as a part of sample characterization were made using the heat capacity option of the Quantum Design Physical Property Measurement System (PPMS) (14 T/0.3 K). This instrument uses a relaxation technique, in which the sample is briefly heated and then allowed to cool. The thermal response of the sample is then fit over the entire temperature response using a model that accounts for the thermal relaxation of both the sample and the sample platform. The samples were attached to the heat capacity
platform with Apezion grease. The thermal response of the platform and grease was measured separately to allow for the subtraction of this component from the final measurement. To achieve maximum accuracy within reasonable time constraints, the system was typically allowed to cool for two time constants. Thermal contact with the environment was minimised by evacuating the sample chamber to approximately 0.01 mTorr. A sample with a flat face is important for these measurements in order to ensure good thermal contact between the platform and the sample. The sample platform used for measurements above 2 K is calibrated and the addenda contributions are subtracted from the measured total specific heat. The typical error in the specific heat measurement is estimated to be < 0.5%.

2.1.8 Raman scattering measurement

Raman scattering or the Raman effect is the inelastic scattering of a photon, discovered by Sir C.V. Raman in liquids and by Grigory Landsberg and Leonid Mandelstam in crystals [80]. When light encounters with the air molecules, the predominant mode of scattering is elastic scattering, called Rayleigh scattering. This scattering is responsible for the blue colour of the sky; it increases with the fourth power of the frequency and is more effective at shorter wavelengths. It is also possible for the incident photons to interact with the molecules in such a way that energy is either gained or lost so that the scattered photons are shifted in frequency. Such inelastic scattering is called Raman scattering. Like Rayleigh scattering, the Raman scattering depends upon the polarizability of the molecules. For polarizable molecules, the incident photon energy can excite vibrational modes of the molecules, yielding scattered photons which are diminished in energy by the amount of the vibrational transition energies. A spectral analysis of the scattered light under these circumstances will reveal spectral satellite lines below the Rayleigh scattering peak at the incident frequency. Such lines are called "Stokes lines". If there is significant excitation of vibrational excited states of the scattering molecules, then it is also possible to observe scattering at frequencies above the incident frequency as the vibrational energy is added to the incident photon energy. These lines, generally weaker, are called anti-Stokes lines.
Thornton and Rex [81] pictured a photon of energy slightly higher than the energy separation of two levels being scattered, with the excess energy released in the form of a photon of lower energy. Since this is a two-photon process, the selection rule is $\Delta J = \pm 2$ for rotational Raman transitions. The energy diagram below (Fig. 2.1.8) is an idealized depiction of a Raman line produced by interaction of a photon with a diatomic molecule for which the rotational energy levels depend upon one moment of inertia. The upper electronic state of such a molecule can have different levels of rotational and vibrational energy. In this case the upper state is shown as being in rotational state $J$ with scattering associated with an incoming photon at energy matching the $J+2$ state.

\[
\Delta E = \frac{\hbar}{2\pi l}(2J + 3)
\]

\[
E_{\text{elect}} = \frac{\hbar^2}{2l}(J + 2)(J + 2 + 1)
\]

\[
E_{\text{elect}} = \frac{\hbar^2}{2l}(J(J + 1))
\]

\[
\nu' = \nu - \frac{\hbar}{2\pi l}(2J + 3)
\]

Fig. 2.1.8 Raman scattering energy schematic.

Since the Raman effect depends upon the polarizability of the molecule, it can be observed for molecules which have no net dipole moment and therefore produce no pure rotational spectrum. This process can yield information about the moment of inertia and hence the structure of the molecule.

In the present study the Raman spectra are collected in backscattering geometry using a 10 mW Ar (488 nm) laser as an excitation source coupled with a Labram-HR800 micro-Raman spectrometer equipped with a 50X objective, appropriate notch filter and a Peltier cooled charge-coupled device detector. For the low-temperature Raman measurements, the samples were mounted on a THMS600 stage from Linkam UK. During
the low-temperature measurements, in the present experimental set up a 1800 g mm\(^{-1}\) grating is used in high-resolution dispersive geometry. In order to achieve very high positional accuracy, the grating was kept unmoved during the entire temperature scan. A spectral window of \(\sim 325\) cm\(^{-1}\) was covered with a positional accuracy of 0.33 cm\(^{-1}\) in such a configuration. The Raman frequencies and Raman line widths were obtained from the best fit to the Lorentzian line shape after baseline correction.

### 2.1.9 Magneto-capacitance measurement

Magnetocapacitance is a property of some dielectric or insulating materials and/or metal-insulator-metal heterostructures that exhibit a change in the value of their capacitance when an external magnetic field is applied to them. Magnetocapacitance can be an intrinsic property of some dielectric materials, such as multiferroic compounds [25]. Magnetocapacitance phenomenon is a characteristic feature for the multiferroic materials which show coupling among the magnetic and ferroelectric order parameters and are known as magnetoelectric multiferroics [35]. For the magneto-capacitance we measure the dielectric constant in the presence of magnetic field. To see the effect of magnetic field on dielectric constant, magnetic field scans are done at constant temperatures. Percentage variation of dielectric constant as a function of temperature is usually performed to show the magneto-capacitive coupling and can be calculated using the following formula:

\[
\left(\frac{\varepsilon'(H) - \varepsilon'(0)}{\varepsilon'(0)}\right) \times 100
\]

(2.1.11)

where \(\varepsilon'(H)\) is the value of dielectric constant in the presence of magnetic field \(H\) and \(\varepsilon'(0)\) is the value of dielectric constant without magnetic field.

In the present study magneto-capacitative effect of the samples has been investigated using a cryogen free low temperature high magnetic field facility. Dielectric constant in the presence of magnetic field was measured using a HP4192 precision LCR meter.
2.1.10 Atomic Force microscopy (AFM)

Atomic force microscopy has been proven a powerful technique for probing the surface of the thin film and deducing valuable information of its topological features [82]. The precursor to the AFM, the scanning tunneling microscope, was developed by Gerd Binnig and Heinrich Rohrer in the early 1980s, a development that earned them the Nobel Prize for Physics in 1986. Binnig, Quate and Gerber invented the first AFM in 1986. AFM operates by scanning a very sharp and tiny tip attached to the end of a cantilever across the sample surface (Fig. 2.1.9). The tip approaches the surface of the sample and interacts with it via Van der Waals forces. The interaction translates in a cantilever deflection or a change in the cantilever’s oscillating frequency, depending on the operational mode of the AFM: contact or tapping. The deflection or the frequency changes of the cantilever are detected by an optical system consisting of a laser beam, which is reflected on the cantilever. The vertical and the horizontal deflections are measured using a split photodiode detector that analyses the reflected beam. The displacement of the cantilever in the three directions is done by means of a piezoelectric scanner, combining independently operated piezo-electrodes, for X, Y and Z direction into a single tube. The two operating modes that have been used, contact-AFM and tapping-AFM, are described in more detail in the following text.

(i) Contact Mode AFM

As we have mentioned the changes in the cantilever’s deflection are monitored with a split photodiode detector as the tip is scanning the sample surface [83], feedback loop maintains a constant deflection between the cantilever and the sample by vertically moving the scanner at each data point to maintain a ‘set-point’ deflection. By maintaining a constant cantilever deflection, the force between the tip and the sample remains constant. The force $F$ is calculated from Hook’s law: $F = -k \cdot x$, where $k$ is the spring constant and $x$ is the deflection. Spring constants usually range from 0.01 to 1.0 N/m, resulting in forces ranging from nN to μN. The distance that scanner moves vertically at each point (x, y) is stored by the computer to form the topographic image of the surface.
(ii) Tapping Mode AFM

In tapping mode, the cantilever is oscillated near its resonance frequency with the amplitude ranging typically from 20 to 100 nm. The tip lightly ‘taps’ the surface while scanning, contacting the surface at the bottom of its swing. The feedback loop maintains constant oscillation amplitude by maintaining a constant RMS of the oscillation signal acquired by the split photodiode detector. In order to maintain constant oscillation amplitude the scanner has to move vertically at each point (x, y). The vertical position of the scanner is stored by the computer, to form the topographic image of the sample surface. In the present work, to study topographic and morphology of the thin films, AFM measurements have been carried out using Nanoscope III a (Digital Instruments).

Fig. 2.1.9. Schematic diagram of Atomic Force Microscope (AFM)
2.1.11 Swift heavy ion (SHI) irradiation

Swift heavy ion (SHI) irradiation experiments have been performed at IUAC, New Delhi using 15 UD tandem accelerator. Details about Pelletron accelerator, materials science beam line (beam line used for irradiation experiment), basic mechanisms involved during ion-solid interaction and models for ion energy loss phenomenon are presented in next subsections.

(i) Pelletron Accelerator

The 15 UD Pelletron, as shown in Fig. 2.1.10, is a versatile, tandem type electrostatic heavy ion accelerator. This is installed in a vertical configuration in an insulating tank of 26.5-meter height and 5.5 meter in diameter. In this machine, negative ions are produced and pre-accelerated to ~ 300 keV by the cesium sputter ion source known as SNICS (Source of Negative Ions by Cesium Sputtering), now it has been replaced by MCSNICS (Multi Cathode SNICS). The pre-accelerated ions are injected into strong electrical field inside an accelerator tank filled with SF₆ insulating gas maintained at a pressure of 6-7 atmospheres. The ion beam is selected by injector magnet, which selects the mass of the ion using mass spectroscopy. The ions are mass analyzed by a dipole magnet called injector magnet and are tuned vertically to downward direction. The ions then enter in the strong electrical field inside the accelerator. A terminal shell of about 1.52 meter in diameter and 3.61 meter in height is located at the center of the tank, which can be charged to a high voltage (~15 MeV) by a pellet charging system. The negative ions on traversing through the accelerating tubes from the column top of the tank to the positive terminal get accelerated. On reaching the terminal, they pass through the stripper (foil or gas), which removes electrons from the negative ions and transforms the negative ions into positive ions with high charge state. For heavier ions (A> 50), the lifetime of the carbon foils used in the stripper are limited to a few hours due to radiation damage. Therefore, a gas filled canal or a combination of the gas stripper followed by a foil stripper is used for heavy ions. The transformed positive ions are then repelled away from the positively charged terminal and are accelerated towards ground potential to bottom of the tank. In this way same terminal potential is used twice to accelerate the ion in tandem. Hence, the name given to this accelerator is a Tandem
Pelletron Accelerator. The final energy of the emerging ions from the accelerator is given by,

\[ E_i = E_{\text{decpot}} + (1 + q_i)V \]

(2.1.12)

where \( E_i \) is the energy of the ions having a charge state \( q_i \) after stripping, \( V \) is the terminal potential in MV and \( E_{\text{decpot}} \) is the deck potential of the SNICS source. On exciting from the tank, the ions are bent into horizontal plane using analyzing magnet. This magnet works as an energy analyzer and depending on the dipole magnetic field, ions of particular energy travel in the horizontal direction. The switching magnet diverts the high-energy ion beam into selected beam line of the beam hall. The ion beam kept centered and focused using steering magnets and quadruple triplet magnets. The beam line of the accelerator is in ultra high vacuum (UHV) condition (~\(10^{-10}\) mbar). The beam is monitored by beam profile meter (BPM) and the current is observed using Faraday cups. The entire machine is computer controlled and is operated from the control room. The accelerator can accelerate ions from proton to uranium from a few MeV to hundreds of MeV (200 MeV) depending on the type of ion.

Fig. 2.1.10: Schematic of the 15UD Pelletron at IUAC, New Delhi, India.
(ii) Materials Science Beam Line

The accelerated beam from the Pelletron accelerator is brought to the beam hall and can be switched to any of the seven beam lines by using the switching magnet. Materials Science beam line is at 15° to the right w.r.t. the zero degree beam line. This beam line has three chambers, namely, high vacuum chamber, ultra high vacuum chamber and goniometer chamber. The high vacuum chamber is a cylindrical shaped multiport stainless steel chamber. A view of the high vacuum chamber is shown in Fig. 2.1.11 (a). The irradiation experiments were performed in high vacuum chamber (~ $10^{-6}$ mbar) at room temperature in materials science beam line (see Fig. 2.1.11(b)). The samples to be irradiated were mounted on the four sides of the target ladder (on copper block). The whole body of the ladder is made of stainless steel and a perforated square copper block is brazed at the end of the ladder. The target ladder is mounted through a Wilson seal mechanism from the top flange of the chamber. This top flange is connected to the chamber through a flexible bellow that can be expanded up to 11 cm from its minimum position. A stepper motor in conjunction with suitable mechanical assembly is used to control the up and down motion of the ladder. The beam on the ladder can be observed by examining the luminescence of the beam on the quartz crystal mounted on all sides of the ladder. After the observation of the beam on the quartz, the sample to be irradiated is brought to the same position as that on the quartz by moving the ladder in the desirable position. A CCD camera is attached to one of the ports of the chamber for viewing the sample and the quartz position. The positions can be monitored using close circuit television (CCTV) in the data acquisition room. The magnetic scanner (that can sweep the beam by 15 mm in y-direction and 15 mm in x-direction) ensures the uniformity of irradiation. A cylindrical enclosure of stainless steel surrounds the sample ladder, which is kept at a negative potential of 120 V. This enclosure suppresses the secondary electrons coming out of the sample during the irradiation. An opening in the suppressor allows the ion beam to fall on the sample. The total number of ions/charges falling on the sample can be estimated by a combination of the current integrator and the pulse counter (Faraday cup) from which the irradiation fluence/dose can be measured.
The counts for the desired ion fluence for each sample can be calculated using the following relation:

\[ \text{No. of counts} = \frac{Dose \times q \times 1.6 \times 10^{-16}}{\text{PulseHeight}} \]  

(2.1.13)

Fig. 2.1.11. An overview of (a) Experimental chamber and (b) materials science beam line at Inter-University Accelerator Center, New Delhi, India.

(iii) Ion Solid Interaction

When an energetic ion passes through the matter, it experiences a series of elastic and inelastic collisions with the atoms which lie in its path. These collisions occur because of the interaction forces between the nucleus and electrons of the projectile and those of the atoms which constitute the solid target. During this collision the energetic ions transfer its energy to nuclei (by elastic atomic collision) and electron (by ionization and excitation) of the target material by two processes:
1. Elastic collision with the target atoms leading to displacement of atoms from their regular lattice sites. This mode of energy transfer is known as nuclear energy loss denoted by \((dE/dX)_n\) or \(S_n\). It is well known mechanism of defect creation in the low energy regime (few eV to 100 keV) and has negligible contribution at high energy regime (1 MeV and above). 

2. Inelastic collision with the target electrons causes their excitation/ ionization. This mode of energy transfer is referred to as electronic energy loss \((dE/dX)_e\) or \(S_e\).

Fig. 2.1.12 shows the schematic of the two mechanisms that occur during the ion solid interaction.

![Fig. 2.1.12. Ion-solid interaction: demonstration of electronic and nuclear energy loss processes during ion solid interaction.](image)

It is well known fact that when a material is bombarded by the heavy ion irradiation, it creates cylindrical damage zones in the material. When SHI passes through the material then material in the vicinity of the ions trajectory may be transformed into a disordered state, giving rise to the so called latent track (damage zone created along the path of the swift heavy ion). In case of SHI irradiation, electronic energy loss is the most considerable energy loss process. The emergence of these traces is the result of local electronic energy deposition along the ion path. Therefore, a number of experimental results have shown that the higher electronic excitations can induce the structural modifications. This implies that all the \(S_e\) dependent effects induced in different materials are probably related to the basic
energy transfer between the incident ions and the target atoms. Two basic models of microscopic energy transfer mechanism, namely thermal spike and the coulomb explosion have been used to establish the relevant parameters governing the basic energy transfer process.

(a) Thermal Spike Model

Thermal spike model is based on the transient thermal process. This model was developed to explain the phase transformation after the SHI irradiation. According to this model the heavy ion irradiation may increase the lattice temperature that induces solid to liquid phase transformation into a localized zone of few nanometer (nm), which is followed by the thermal quenching \(10^{13}\) K/s of a cylindrical molten liquid along the ion track. This results in the formation of highly disordered or amorphized latent track. The threshold value for the creation of the latent tracks is associated with the energy needed to induce a liquid phase along the ion path [84, 85].

In this process, the incoming ion gives its energy to the electron gas in \(\sim 10^{-17}\) sec which is calculated from the collision time of ion with electron. The local thermalization in electronic system will take \(10^{-15}\) sec to complete. Heat transfer from the electronic to atomic subsystem becomes substantial between \(10^{-14}\) to \(10^{-12}\) sec depending on the magnitude of the coupling (electron-electron coupling and electron-phonon coupling) between the subsystems. The electron-phonon coupling implies the ability of electrons to transfer their energy to the lattice.

(b) Coulomb Explosion Model

In the Coulomb explosion model [86-87], it is assumed that the incoming ions scatter the target electrons and create a column/cylinder of ionized atoms and the excited electrons are ejected by the Coulomb repulsion. The electron excitation energy is rapidly shared with other electrons via electron-phonon (e-ph) interaction. The mutual Coulomb repulsion of the ions produces atomic displacements leading to a dense cloud of interstitial atoms and vacancies along the original ion trajectory. This model seems to be well suited for the insulating materials. In metals, which have large electronic mean free path, the free electrons
carry away the excitation energy so efficiently that the sample warms up as a whole without considerable atomic motion.

In the present work, the thin films of the BiMn$_2$O$_5$ multiferroic samples deposited on LaAlO$_3$ (LAO) substrate have been irradiated with 200 MeV Ag$^+$ ions. The Ag ions were selected to create the columnar defects. In fact, the defect morphology depends upon threshold value of the particular material to be irradiated [88]. The electronic energy loss, $(\text{dE/dx})_e$, of the 200 MeV Ag ion beam for the same samples is about 14.25 keV/nm, which is larger than the $S_{\text{eth}}$. Therefore, there is a possibility of creation of columnar defects/tracks in the materials. The variation of $(\text{dE/dx})_e$ and $(\text{dE/dx})_n$, calculated using SRIM code for 200 MeV Ag ions incident in BiMn$_2$O$_5$ is shown in Fig. 2.1.13.

![Graph](image.png)

Fig. 2.1.13. Variation of $(\text{dE/dx})_e$ and $(\text{dE/dx})_n$ versus energy in BiMn$_2$O$_5$ for 200 MeV Ag ions.
2.2 Theoretical Formalisms

2.2.1 Theory of specific heat and anhormonic corrections

The specific heat in general is defined by $\frac{dQ}{dT}$ and unless stated otherwise, will be assumed to refer to 1 gm of molecule of the solid. However unless one specifies in which way the increase in temperature takes place, the specific heat is undetermined; in particular one must specify the corresponding change in volume. Thus, there exist an infinite number of specific heats, but in general one is interested in only two; specific heat at constant volume $C_v$ and specific heat at constant pressure $C_p$. $C_v$ can be calculated as

$$C_v = \left( \frac{dQ}{dT} \right)_v = \left( \frac{\partial E}{\partial T} \right)_v$$

Theoretically speaking, this is the most interesting quantity, as it is obtained immediately from the energy of the system. From the experimental point of view, however, it is more convenient to measure the specific heat of a solid at constant pressure than at constant volume.

From the atomic point of view one may distinguish between various contributions to the specific heat of solids. In the first place, there is the contribution resulting from the atomic vibrations in the crystal; an increase in temperature is associated with a more vigorous motion of the atoms, which require an input of energy. Second, in metals and in semiconductors there is an additional contribution to the specific heat from the electronic system. Usually this contribution is small relative to that of lattice contributions. As the temperature is raised from the absolute zero, the specific heat increases rather rapidly from zero and finally levels off to a nearly constant value. For a solid having same type of atoms, the value at high temperature is about 6 cal mole$^{-1}$degree$^{-1}$. This is known as the law of
Dulong and Petit. Anomalies in the specific heat curves are observed in the magnetic metals; for example in nickel, iron and cobalt, a peak is observed in the vicinity of magnetic transition temperature. This is true for any kind of solids, viz. inter-metallic, oxides etc. The height of the peak is of the same order of magnitude as the normal specific heat. The peak is associated with the transitions from the ordered (ferromagnetic) to the disordered (paramagnetic) state. Similar peaks occur in the specific heat of alloys which exhibit order-disorder transitions, and in the ferroelectric materials.

In case of pure and Ti doped multiferroic BiMn$_2$O$_5$ system, these are insulators so we neglect the electronic contributions and the analysis is focused on the lattice contribution as well as the contributions due to magnetic and ferroelectric ordering in the system. In order to confirm the magnetic and ferroelectric contribution in any kind of system, the best approach is always other way round i.e. calculation of lattice contribution by considering the non-magnetic analog to the system and subtraction of lattice contribution from the total measured specific heat.

There are various theories of the lattice specific heat. The vibrational energy of a crystal containing N atoms is equivalent to the energy of a system of 3N harmonic oscillators. This feature is common to all theories of the specific heat and the distinction between the various theories is based on their differences in the proposed frequency spectrum of the oscillators. The central problem in the theory of the specific heat is therefore the calculation of the wavelengths and frequencies of the possible modes of vibration of the crystal under consideration.

For the harmonic oscillator representation referred above, the following qualitative remarks may provide some clarification. Suppose, it was possible to fix the position of all the nuclei in a crystal such that they all in their equilibrium position. If one of the nuclei was now displaced over a distance small compared to the shortest interatomic distances, and then set free again, the displaced atom would carry out harmonic vibrations about its equilibrium position and the energy would be same as that of three one-dimensional harmonic oscillators. Applying the same reasoning to other atoms in the crystal, one arrives at a
system of 3N harmonic oscillators representing the vibrations of the crystal as a whole. The
energy of a harmonic oscillator of natural angular frequency $\omega$ may be written as;

$$\varepsilon = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}$$  \hspace{1cm} (2.2.2)

Where the first term on the right represents the kinetic energy (p is the momentum) and the
second term represents the potential energy (q is the deflection from equilibrium position). It
is well known that the average energy of a harmonic oscillator according to classical
statistical mechanics is given by

$$\langle \varepsilon \rangle = \int_0^\infty \varepsilon e^{-\varepsilon/kT} d\varepsilon / \int_0^\infty e^{-\varepsilon/kT} d\varepsilon = kT$$  \hspace{1cm} (2.2.3)

Where T is the absolute temperature and k is the Boltzmann’s constant. It is important to
mention here that the frequency does not enter in this result. In other words, the vibrational
energy of a crystal of N atoms is;

$$E = 3NkT$$  \hspace{1cm} (2.2.4)

independent of the frequency distribution of the oscillator used in the model. Now, as long
as the volume/pressure is kept constant, eq (2.2.4) is the only temperature dependent
contribution to the total energy of the system. Thus, for a solid containing one type of atoms
and putting N equal to Avogadro number, one obtains for specific heat per gram atom,

$$C = 3Nk = 3R = 5.96 \text{ cal degree}^{-1} \text{ mole}^{-1}$$  \hspace{1cm} (2.2.5)

where R is the gas constant. Similarly, if the solid consists of N atoms of type A and N
atoms of type B, the specific heat per mole would be 6R, etc. The result obtained is in
quantitative agreement with experiment (if sources of the specific heat other than lattice
vibrations are subtracted) at high temperatures only. In other words, it does not explain the
decrease of the specific heat at low temperatures, as observed for all solids. This discrepancy
is essentially removed when quantum theory is used. Now we will discuss about the
quantum theory treatment to the specific heat using Debye and Einstein approximation.
The common approach to the phonon part of molar specific heat is usually limited just to the harmonic term within the Debye approximation written in the form [89]

\[ C_{phD} = 9Nk_B \left( \frac{T}{\theta_D} \right) \int_0^{\theta_D} x^4 \frac{\exp(x)}{[\exp(x) - 1]} \, dx \]  \hspace{1cm} (2.2.6)

where \( x_D = \theta_D / T \) and \( k_B \) is the Boltzmann constant. In this case, when there are 8 atoms/f.u., \( N \) is taken as \( 8N_A \) and the high-temperature limit yields \( C_{ph} = 24R \) (\( R \) is the gas constant), which is the Dulong-Petit law. Such approach to the phonon part of specific heat in this class of intermetallics usually leads to the high Debye temperature \( \theta_D \) values. We have observed, however, that this approach is not sufficient to explain fully the specific heat data of \( \text{BiMn}_2\text{O}_5 \).

When one considers a temperature dependent \( \theta_D \), in this case a better agreement with the low-temperature part of the specific heat data is obtained. Nevertheless, the description of the high-temperature data remains unsatisfactory and, moreover, the temperature dependence of the Debye temperature is unrealistic.

The best description of the low temperature part of the phonon specific heat has been achieved by considering the splitting of the phonon spectrum into the acoustic and optical branches. The acoustic branches are then described by the Debye formula and for the optical branches the Einstein’s approximation can be expressed in the form [89]

\[ C_{phE} = R \sum_{\ell=1}^{\ell} x_{\ell}^2 \frac{\exp(x_{\ell})}{[\exp(x_{\ell}) - 1]^2} \]  \hspace{1cm} (2.2.7)

where \( x_{\ell} = \theta_{\ell} / T \) and \( \theta_{\ell} \) is the characteristic Einstein temperature of each optical branch.

In the present case of \( \text{BiMn}_2\text{O}_5 \), the lattice contribution has been obtained by fitting the data to two Einstein optical modes, one associated with the Bi - Mn atoms and the other with the O atoms. The oscillator corresponding to the Bi - Mn atoms is centered at \( \theta_{\ell_1} \) and the other at \( \theta_{\ell_2} \). The estimation of the lattice contribution is carried out by trial and error, where the temperature regions of the data used for the fitting are adjusted until valid results are
obtained. In order to avoid the contribution of magnetic anomaly, the data near to the magnetic anomaly (∼39 K) is not used (we have left the 5 to 45 K region). This description gives the best fit in the low-temperature part of the specific heat, say up to 100 K. At higher temperatures, the difference between the fit and the experimental data was found to increase. As the temperature approaches to room temperature, the phonon part of specific heat exceeds the Dulong-Petit limit, which indicates that it cannot be described within the harmonic approximation. Because of this, one has to include the anharmonic terms into the analysis of the phonon part of specific heat. These anharmonic corrections are small but not negligible and, in general, add a linear temperature contribution to $C_{ph}$ at high temperatures. We have selected the approximation described in detail by C.A. Martin [90]. In this approximation, the phonon spectrum is again described by the modified Einstein formula. Then the resulting isobaric phonon specific heat can be written in the form

$$C_{ph} = R \sum_{\omega_{i}} \frac{1}{1 - \alpha_{E_{i}} T} \frac{x_{i}^{2} \exp(x_{E_{i}})}{[\exp(x_{E_{i}}) - 1]^{2}}$$

(2.2.8)

where $\alpha_{E_{i}}$ is the anharmonic correction coefficient for optical model. The estimated lattice contribution for BiMn$_{2}$O$_{3}$ is considered to be same for Ti doped samples in nonmagnetic approximation. The excess specific heat ($C_{total} - C_{lattice}$) is then obtained by subtracting the lattice contribution from the measured specific heat.

2.2.2 Extraction of crystallographic data from powder x-ray diffraction data using Rietveld refinement method

It was Rietveld (i) who first worked out computer based analytical procedures (quite sophisticated for the time, as it turned out) to make use of the full information content of the powder pattern, (ii) who put them in public domain by publication of two seminal papers.
(1967, 1969) [91] and (iii) very importantly, freely and widely shared his computer program. It is for these reasons that the method is appropriately referred to now as 'the Rietveld method', or 'Rietveld refinement', or 'Rietveld analysis'. In the Rietveld method the least-square refinements are carried out until the best fit is obtained between the entire observed powder diffraction pattern taken as a whole and the entire calculated pattern based on the simultaneously refined models for the crystal structures, diffraction optics effects, instrumental factors and other specimen characteristics (e.g. lattice parameters) as may be desired and may be modelled. A key feature is the feedback during refinement, between improving knowledge of the structure and improving allocation of observed intensity to partially overlapping individual Bragg reflections [92].

The quantity minimized in the least-squares refinement is the residual, \( S_y \);

\[
S_y = \sum_i w_i (y_i - y_{ei})^2
\]  

(2.2.9)

where \( w_i = 1/y_i \)

\( y_i \) = observed (gross) intensity at the \( i^{th} \) step

\( y_{ei} \) = calculated intensity at the \( i^{th} \) step,

and sum over all the data points.

It is crucial feature of Rietveld method that no effort is made in advance to allocate observed intensity to particular Bragg reflections nor to resolve overlapped reflections. Consequently, a reasonably good starting model is needed. The method is structure refinement method. It is not a structure solution method.

Typically, many Bragg reflections contribute to the intensity, \( y_i \), observed at any arbitrarily chosen point, \( i \), in the pattern. The calculated intensities \( y_{ei} \) are determined from the \( |F_i|^2 \) values calculated from the structural model by summing of the calculated contributions from neighbouring (i.e. within a specified range) Bragg reflections plus the background.
\[ y_i = S \sum_k L_k |F_k|^2 \phi(2\theta_i - 2\theta_k) P_k A + y_{bi} \]  

(2.2.10)

where

- \( S \) is the scale factor
- \( K \) represents the miller indices, \( h, k, l \), for Bragg reflections
- \( L_k \) contains the Lorentz, polarization and multiplicity factor
- \( \phi \) is the reflection profile function
- \( P_k \) is the preferred orientation
- \( A \) is an absorption factor
- \( F_k \) is the structure factor for the \( K \)th Bragg reflection and
- \( y_{bi} \) is the background intensity at the \( i \)th step.

The least square minimization procedures lead to a set of normal equations involving derivatives of all the calculated intensities, \( y_i \), with respect to each adjustable parameter and are soluble by inversion of the normal matrix with elements \( M_{jk} \) formally given by

\[ M_{jk} = -\sum_i 2w_i \left[ \frac{\partial^2 y_i}{\partial x_j \partial x_k} \right] \]  

(2.2.11)

where the parameters \( x_j, x_k \) are the adjustable parameters. In this algorithm, it is common practice to approximate the matrix elements by deletion of the first term, that is \( (y_i - y_{ci}) \).

One is thus dealing with the creation and inversion of an \( m \) by \( m \) matrix, where \( m \) is the number of parameters being refined. Because the residual function is non-linear, the solution must be found with an iterative procedure in which the shifts \( \Delta x_k \), are

\[ \Delta x_k = \sum_j M^{-1}_{jk} \frac{\partial S_j}{\partial x_k} \]  

(2.2.13)
The calculated shifts are applied to the initial parameters to produce an improved model and the whole procedure is then repeated. Because the relationships between the adjustable parameters and the intensities are non-linear, the starting model must be close to the correct model or the non-linear least square procedure will not lead to a global minimum. Rather, the procedure will either diverge or lead to a false minimum if the starting point is in its domain. (This is true for all non-linear least-square refinements, not just Rietveld refinement).

In general, it is important to judge, whether to keep a parameter turned on for refinement as one proceeds to turn on the following parameters, or to turn it off to prevent the refinement from 'blowing up.' Simultaneous refinement of highly correlated parameters causes this problem and must be avoided. For example, occupancies and displacements parameters should not be simultaneously refined. Similarly, the overall scale factor should not be refined at the same time as the occupancy factors of all of the atoms. One among these parameters must be fixed. Also, it is important to refine the parameters most uncorrelated with other parameters first. The refinement strategy suggested in Young's "Rietveld Method" [92] is

1. Scale factor - stable
2. Specimen displacement - stable
3. Flat background - stable
4. Lattice parameters - stable
5. More background - stable
6. W, in the Caglioti function for peak widths-poorly stable
7. x, y, z (atomic coordinates) - fairly stable
8. Occupancies and isotropic (thermal) displacement parameters - not generally stable
9. U, V, (in the Caglioti function) and other profile parameters - not generally stable
10. Anisotropic (thermal) displacement parameters - not generally stable
11. Zero point – stable

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In most cases it is not very meaningful to refine anisotropic displacement parameters using conventional X-ray diffraction data. One must limit the refinement to isotropic parameters in order to prevent the displacements of the atoms from becoming 'non-positive definite'.

There are various programs available for the Rietveld refinement method, we have used the FullProf program, which is based on the code of the DBW program. This, in turn, is also a major modification of the original Rietveld-Hewat program. An early version is discussed in the Young and Wiles article published in J. Appl. Cryst. [93] and described in the user's guide distributed by R.A. Young.

Features of FullProf program

Some of the most important features of FullProf program are summarised below:

- X-ray diffraction data: laboratory and synchrotron sources.
- Neutron diffraction data: Constant Wavelength (CW) and Time of Flight (TOF).
- One or two wavelengths (eventually with different profile parameters).
- The scattering variable may be \(2\theta\) in degrees, TOF in microseconds and Energy in KeV.
- Background: fixed, refinable, adaptable, or with Fourier filtering.
- Choice of peak shape for each phase: Gaussian, Lorentzian, modified Lorentzians, pseudo-Voigt, Pearson-VII, Thompson-Cox-Hastings (TCH) pseudo-Voigt, numerical, split pseudo-Voigt, convolution of a double exponential with a TCH pseudo-Voigt for TOF.
- Multi-phase (up to 16 phases).
- Preferred orientation: two functions available.
- Absorption correction for a different geometries. Micro-absorption correction for Bragg-Brentano set-up.
- Choice between three weighting schemes: standard least squares, maximum likelihood and unit weights.
Choice between automatic generation of hkl and/or symmetry operators and file given by user.

Magnetic structure refinement (crystallographic and spherical representation of the magnetic moments). Two methods describing the magnetic structure in the magnetic unit cell for making use of the propagation vectors using the crystallographic cell. This second method is necessary for incommensurate magnetic structures.

Automatic generation of reflections for an incommensurate structure with up to 24 propagation vectors. Refinement of propagation vectors in reciprocal lattice units.

hkl-dependence of (full width at half maximum) FWHM for strain and size effects.

hkl-dependence of the position shifts of Bragg reflections for special kind of defects.

Profile Matching. The full profile can be adjusted without prior knowledge of the structure (needs only good starting cell and profile parameters).

Quantitative analysis without need of structure factor calculations.

Chemical (distances and angles) and magnetic (magnetic moments) slack constraints. They can be generated automatically by the program.

The instrumental resolution function (Voigt function) may be supplied in a file. A microstructural analysis is then performed.

Form factor refinement of complex objects (plastic crystals).

Structural or magnetic model could be supplied by an external subroutine for special purposes (rigid body TLS is the default, polymers, small angle scattering of amphiphilic crystals, description of incommensurate structures in real direct space, etc).

Single crystal data or integrated intensities can be used as observations (alone or in combination with a powder profile).

Neutron (or X-rays) powder patterns can be mixed with integrated intensities of X-rays (or neutron) from single crystal or powder data.

Full Multi-pattern capabilities. The user may mix several powder diffraction patterns (eventually heterogeneous: X-rays, TOF neutrons, etc.) with total control of the weighting scheme.
Montecarlo/Simulated Annealing algorithms have been introduced to search the starting parameters of a structural problem using integrated intensity data.

Unit cell schematic representation

Crystallographic parameters refined from powder x-ray diffraction data using Rietveld refinement technique have been used to draw the unit cell structure of BiMn$_2$O$_5$. FullProf program provides the .cif file as a output file, which has been used as a single input file in Jmol program to get a unit cell schematic in the form of polyhedrons. Jmol program is freely available at Inorganic Crystal Structure Database (ICSD) web site [94]. Let us know, what are cif and Jmol.

What is CIF?

The CIF format is the standard defined by the IUCr. It is advised to check the CIF file using one of the free CIF syntax checkers e.g. (chemistry and crystallography department at Cambridge) CCDC's free Encifer. One should in particular check the symmetry operations, for example by using CCD's Mercury molecular plotting application. Some journals (eg IUCr's Acta Cryst) publish the original CIF files, and these should be used when available rather than these CIF files re-generated from the ICSD data.

What is Jmol?

Jmol is a Java application for embedding interactive 3D crystal structures within a Web page. One should have Java Runtime Environment (JRE) installed in the machine. Jmol can display anisotropic thermal vibration matrices $U_{ij}$ or $B_{ij}$.